APPLICATION

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TITLE: SILICON-CONTAINING RESIST SYSTEMS WITH CYCLIC KETAL PROTECTING GROUPS

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5 **SILICON-CONTAINING RESIST SYSTEMS WITH CYCLIC KETAL PROTECTING GROUPS**

BACKGROUND OF THE INVENTION

10 The need to remain cost and performance competitive in the microelectronics industry has caused continually increasing semiconductor device density in integrated circuits. To facilitate the increase in device density, new technologies are constantly needed to allow the minimum feature size of these semiconductor devices to be reduced. This requires high-resolution lithography, the principal

15 technique used in patterning microelectronics circuitry. Over approximately the last 20 years, the industry has migrated to shorter wavelength photolithography as the primary means of scaling the resolution to sustain the progressive demand for smaller features. The wavelength of photolithography has migrated from mid-ultraviolet (MUV) wavelengths (350–450 nm) to deep-UV (DUV) radiation (190-

20 300 nm) and vacuum UV (VUV, 125-160 nm). Likewise the photosensitive materials used in photolithography, known as resists, have evolved. MUV lithography employed diazonaphthoquinone (DNQ) and novolac-based resists. These materials offered high performance but were not extendible to DUV and VUV wavelengths due to their opacity at these shorter wavelengths. In addition,

25 these resists were not of sufficient sensitivity to afford high throughput manufacturing.

In response to the need for new, lower opacity, higher sensitivity materials for DUV imaging, chemically amplified resists (CARs) have been developed (e.g.

30 see Ito et al., US 4,491,628) based on photochemically-generated acid-catalyzed deprotection of an acid-labile polymer or resin. For positive tone CARs, acid labile moieties of the polymer are cleaved by an acid-catalyzed thermolysis reaction that renders the deprotected form of the polymer soluble in a subsequently applied developer, such as an aqueous base. The acid becomes

35 available from a radiation sensitive or photosensitive acid generator component.

5   The acid-labile polymer is prepared from an alkali-soluble resin which have
     aqueous-soluble moieties, such as a fluorocarbinol. The alkali-soluble resin is
     partially protected with acid labile groups such as an acetal, an orthester, a ketal
     or other protecting groups. The protection converts the soluble hydroxyl group to
     an insoluble group by converting a large portion of hydrophilic hydroxyl groups to
10   more hydrophobic groups (such as ketal groups), resulting in a drastic decrease
     in the dissolution rate of the polymer in an aqueous-base developing solution.
     The extent of inihibition of the polymer to dissolution in the developer depends on
     the quantity of protecting groups grafted on to the polymer chain. It also depends
     on the inhibiting characteristics of the protecting groups. A group having lower
15   polarity would have the effect of diminishing the solubility of the polymer in an
     aqueous alkaline developer. The shape and size of the protecting group would
     also affect its inibition by means of its ability to block the developer from coming
     into close contact with the unprotected hydroxyl group for dissolution.

20   An image of the projected patternwise radiation is formed in the resist film after
     development, which can then serve as an etch-resistant mask for subsequent
     pattern transfer steps. The resolution obtained is dependent on the quality of the
     aerial image and the ability of the resist to maintain that image.

25   The resolution, R, of an optical projection system such as a lithography stepper is
     limited by parameters described in Raleigh's equation:

$$R = k \, \lambda/NA,$$

     where λ represents the wavelength of the light source used in the projection
     system and NA represents the numerical aperture of the projection optics used.
30   "k" represents a factor describing how well a combined lithography system can
     utilize the theoretical resolution limit in practice and can range from about 0.85
     down to about 0.35 for standard exposure systems. The theoretical dimensional
     limit of equal-sized half-pitch features is one quarter of the wavelength, λ. (k =
     0.25) when NA = 1, as the dose applied to the resist is equal to the square of the
35   intensity, and thus the resolution cannot be modulated by any more than $\lambda/4$, or a

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5   pitch of λ/2. The resolution attainable with each advancing generation of
materials has been extended toward these limits through the use of low k
techniques and high numerical aperture tools. For 157 nm lithography, the latest
VUV wavelength being developed for manufacturing, and using a very high but
potentially manufacturable NA of 0.95, the minimum k factor (i.e. λ /4) equals ~40

10   nm. To obtain images below this feature size, either an extension of NA to >1,
such as is afforded with immersion lithography, or with a non-diffraction limited,
non-optical lithography system, such as the so-called next generation lithography
(NGL), are options. The most promising of these NGLs are extreme ultraviolet
(EUV, sometimes referred to as soft x-ray) or electron beam lithography (EBL).

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As the desired feature size decreases, the resolution capability of many current
resists is not sufficient to yield the smaller features. The need to achieve less
than 100 nm resolution has prompted a push toward increasing numerical
aperture (NA) exposure tools. The higher NA allows for improved resolution of

20   smaller feature sizes, however, the higher NA also reduces the depth of focus of
aerial images projected onto the resist film. When the depth of focus is relatively
shallow, the thickness of the resist film becomes a factor in achieving proper
exposure. Thus, thinner resist films may be required for proper exposure at high
resolution, but such films often do not yield acceptable overall performance,

25   especially when considering etch requirements for the underlying substrate.

As the resist film is thinned to account for the higher NA, the resist becomes less
suitable as an etch mask against later processing of the underlying
semiconductor substrate. For example, since the resist film is thin, variation in

30   thickness becomes more significant and may introduce defects into subsequent
devices formed on the substrate. Also, micro-channels often form in the upper
portions of a resist layer during transfer of the resist image to the substrate by
etching. When the resist layer is thin, the micro-channels may extend to the
underlying substrate, rendering the resist less effective as a mask.

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5   In addition, the process latitude of many current resists is not sufficient to consistently produce the smaller desired features within specified tolerances. Some of the process parameters where variance may be difficult to avoid include bake time and temperature, exposure time and source output, aerial image focus, and develop time and temperature. The process latitude of a resist is an

10   indication of how wide such variations can be without resulting in a change in the resolution and/or image profile (i.e., size and/or shape of a resist image). That is, if the process latitude is sufficiently wide, then a process parameter may vary, but the variance will not produce a change in the resist image incompatible with specified tolerances.

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     Another problem that occurs as feature size decreases and pattern density increases, is that collapsing of such high aspect ratio features in the resist may occur. Thus, a thinner resist layer may be required to minimize image collapse.

20   One approach that enables the use of higher NA exposure tools as well as a thinner photoresist film is multilayer resist processing. One type of multilayer resist processing uses a bilayer (two layer) imaging scheme by first casting a highly energy absorbing underlayer on the semiconductor substrate then casting a thin, silicon-containing imaging layer (photoresist film) on top of the underlayer.

25   The silicon-containing resist provides good etch selectivity for anisotropic dry etch processing, such as reactive ion etch (RIE) using an oxygen-containing plasma. Next, selected portions of the silicon-containing layer are exposed and developed to remove the unexposed portions of a negative photoresist film or the exposed portions of a positive photoresist film. Generally, the underlayer is

30   highly absorbing at the imaging wavelength and is compatible with the imaging layer. Interactions to be considered include adhesion between the two layers, intermixing, and contamination of the imaging layer by the components of the underlayer. Also, the refractive index of the underlayer is matched to the refractive index of the silicon-containing resist layer to avoid degrading the

35   resolution capability of the silicon-containing resist.

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Conventional underlayers include diazonapthoquinone (DNQ)/novolac resist material or novolac resin cast on the semiconductor substrate. The underlayers are typically selected to have good selectivity for an anisotropic etch, and to be sufficiently rigid to minimize feature collapse.

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For the imaging layer, resists containing a wide variety of silicon-containing polymers have been used, including silsesquioxane, silicon-containing acrylics, silanes, etc. Among the several possible silicon-containing polymers, aqueous base-soluble silsesquioxane polymers, such as poly(p-

15   hydroxybenzylsilsesquioxane) (PHBS), have emerged as the most promising candidates for silicon-containing polymers in bilayer resist systems. Unfortunately, although promising, phenolic polymers, such as PHBS, have transparency limitations. The phenolic polymers used in 365 nm and 248 nm wavelength lithographic processes do not provide sufficient transparency for 193

20   nm and 157 nm lithographic processes to produce vertical profiles on the resist images. For example, prior art phenolic polymers have extremely high absorption in the range of 10 μm^{-1} at 193nm. Newer polymers have been investigated, including the use of bi- and tri-cyclic structures and fluoroalkyl moieties to improve transparency at 193 nm and 157 nm wavelengths.

25

A phenomenon known as image blur diminishes the integrity of the pattern (Hinsberg et al., *Proc. SPIE*, 2000, *3999*, 148 and Houle et al., *J. Vac. Sci. Technol B*, 2000, *18*, 1874). Image blur can be defined as the deviation of the developable image from that of projected aerial image which is transferred into

30   the film as the concentration of photochemically generated acid. While accelerating the rate of the deprotection reaction, the application of thermal energy diminishes the fidelity of the aerial image of acid formed during the patternwise exposure. Image blur can be divided into two contributing factors: gradient-driven acid diffusion and reaction propagation. Both factors contribute

35   to blur, but to different degrees and with different temperature dependence.

5   The first factor contributing to image blur is often referred to as acid diffusion and can be described by Fickian diffusion models for solids (Hinsberg, 2000). Choice of the photoacid being generated from the photoacid generator (PAG) and the mobility in the chosen polymer matrix dictate this factor. The mobility in the

10   polymer matrix is dependent on the comprising chemical functionality of the polymer, the free volume of the matrix, the glass transition temperature (T_g) of the polymer and the temperature and time of baking steps encountered during the resist processing. Processing at temperatures above T_g will tend to increase image blur. Therefore, a higher T_g is often desired to avoid blur-inducing film

15   instability. Higher T_g is typically achieved by providing longer cyclic chains in the side groups. Although longer cyclic chains tend to decrease the transparency of the resist formulation at the wavelengths of interest, the addition of fluorine in the polymer structures can improve transparency.

20   A second contributing factor to image blur is sometimes described as reaction propagation (Hinsberg, 2000; Houle, 2000) and is best described by Arhenius behavior. Activation energy (enthalpy, hereinafter referred to as E_a), volatility of products (entropy), and the availability and concentration of deprotection-reaction-dependent co-reactants such as moisture dictate the degree to which

25   the reaction propagates away from the original acid profile. Higher E_a for the deprotection reaction requires higher baking temperatures, which will tend to increase image blur. Current resists for 193 nm lithography have relatively high E_a (i.e. greater than about 20 kcal/mol).

30   In order to achieve high resolution, high sensitivity and high degree of process latitude, both image blur factors must be eliminated or minimized. Both of these contributing factors can be tempered by the addition of acid-quenchers, or bases, which have been shown to reduce image blur. Additionally it has been recognized that image blur is temperature dependent, and tends to increase as

35   processing temperature increases. Breyta et al. disclose that appropriate baking

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5   conditions can optimize the resolution attainable with CARs in US Patent
     6,227,546. However, since the extent of thermally induced image blur has been
     estimated to be on the order of 10-50 nm with conventional resist processing
     schemes by various researchers (Hinsberg 2000; Houle 2000; Krasnaperova et
     al., *J. Vac. Sci. Technol. B*, 1994, *12*, 3900; Lin et al, *Science* 2002, *297*, 372),
10   processing that reduces this phenomenon further are desirable.

     The use of protecting groups that have low activation energy for the acid-
     catalyzed cleaving may help reduce image blurring. Low activation energy
     protecting groups, such as acetal, ketal and orthoesters, have been used.
15   However, prior art low activation protecting groups exhibit the problem that they
     generate undesirable deprotected species which render process control difficult.
     For example, chemically amplified photoresist compositions based on acid labile
     groups comprising acetals often give rise to unpredictable results. In particular,
     photoresist components comprising an acetal moiety designed to produce a
20   hydroxylic moiety imparting base solubility to the resist typically yield aldehydes
     upon acid catalyzed cleavage or hydrolysis. In turn, such aldehyde species may
     lead to resist crosslinking by means of aldol condensation reactions under the
     influence of heat or radiant energy from the exposing radiation source. Thus,
     many such acetal based resists unpredictably demonstrate both positive tone
25   and negative tone behaviors. Furthermore, known photoresist compositions
     based on acetal acid labile groups exhibit a cleavage reaction rate of some
     nominal value in the exposed regions even at ambient temperature, which
     reaction rate is accelerated during a PEB step. The cleavage reaction may also
     continue at a slow rate following PEB and prior to development. If such
30   compositions are processed without the use of a PEB, competing contact
     reactions or reactions with environmental contaminants slow and interrupt the
     cleavage reaction prior to completion of acetal cleavage sufficient to render the
     composition differentially soluble, thus acceptable relief images can not be
     obtained. If such compositions are processed with the use of a PEB, the degree
35   of completion of the cleavage reaction varies highly depending upon the variation

5   in delay time between the exposure step and the PEB step, and also depending upon the remaining, unconsumed acid present in the resist at the commencement of the PEB step. For these reasons, the results are unpredictable. Thus, there is a need for improved chemically amplified photoresist compositions which are not subject to adverse reactions with

10   environmental contaminants and which are tolerant of variable or lengthy delays between exposure and the post exposure bake step, if any, or between the PEB step and development.

Orthoester protecting groups are relatively highly reactive, and the self life of the

15   resist product would be limited.

Ketal protecting groups typically have higher reaction rates in comparison to acetal systems, for example, up to a thousand times faster. Therefore, the acid catalyzed deprotection reaction may occur at room temperature almost

20   immediately, while the deprotection reaction in acetal systems will require several hours at room temperature, or will require post-exposure bake (PEB). Resist systems using ketal protecting groups may be acid catalyzed without PEB, or at low PEB, and will retain the aerial image without degradation. Since most silsesquioxane (SSQ) systems have a low T_g, the use of a ketal protecting group,

25   which has low PEB or no PEB characteristics, provide flexibility in designing the polymer structure and usually enhances the lithographic performance. However, prior art ketal protecting groups are typically linear ketal groups, which have the disadvantages of having low inhibition characteristics and relatively short shelf life.

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Thus, there is a need for improved silsesquioxane polymers structures useful in photoresist compositions and in photolithography processes, that have low activation energy for the acid-catalyzed cleaving, as well as improved inhibition of the protected polymer towards a developer, and increased resist shelf life.

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5   SUMMARY OF INVENTION

It is an objective of the present invention to provide a photoresist or resist composition containing a silisesquioxane polymer that has high resolution.

10   It is a further objective of the present invention to provide a resist composition that includes a silisesquioxane polymer having cyclic ketal pendant solubility inhibiting acid-labile moieties that have low activation energy for the acid-catalyzed cleaving or deprotection reaction.

15   It is yet another objective of the present invention to provide a photolithographic method of forming a structure on a substrate that is effective at wavelengths 193 nm and below to provide high resolution transfer of patterned images.

The present invention provides silsesquioxane polymers that are useful in
20   photoresist compositions, and more particularly in positive resist compositions, and photolithographic imaging methods for using such resist compositions. The inventive lithographic imaging methods are particularly useful in the manufacture of integrated circuits or other similarly patterned structures of very high resolution, patterned structures.
25

Accordingly, the present invention provides a resist composition that includes an acid-sensitive imaging polymer and a radiation-sensitive acid generator, wherein the imaging polymer contains a silsesquioxane backbone and a solubility inhibiting pendant cyclic ketal acid-labile moiety having a low activation energy
30   for acid-catalyzed cleaving, and wherein at least a portion of the imaging polymer is fluorinated.

In another aspect of the present invention, the imaging polymer in the inventive resist composition also includes a pendant solubility promoting moiety.
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5   The present invention is directed to a method of forming a structure on a substrate, including the steps:

(a) providing a substrate;

(b) applying a resist composition to the substrate to form a resist layer on the substrate, wherein the resist composition includes (i) an acid-sensitive

10   imaging polymer, and (ii) a radiation-sensitive acid generator, wherein the imaging polymer contains a silsesquioxane backbone, and a solubility inhibiting pendant cyclic ketal acid-labile moiety having a low activation energy for acid-catalyzed cleaving and wherein at least a portion of the imaging polymer is fluorinated;

15   (c) patternwise exposing the substrate to radiation, whereby acid is generated by the radiation-sensitive acid generator in exposed regions of the resist layer;

(d) removing patternwise soluble portions of the resist layer to form a pattern of spaces in the resist layer; and

20   (e) transferring the pattern of spaces to the substrate.

Optionally, the method may also include baking the exposed resist layer to promote an acid-catalyzed reaction in exposed portions of the resist layer subsequent to exposure (post-exposure bake or PEB).

25

In yet another aspect of the present invention, the lithographic method is a multilayer method, wherein a planarizing layer is formed over the material layer, and the resist layer is applied directly to the planarizing layer.

30   According to another aspect of the invention, the step of transferring the pattern to the material layer may include any of depositing, plating, implanting or etching the substrate through the pattern of spaces.

The foregoing and other features and advantages of the invention will be

35   apparent from the following detailed description of the invention.

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DETAILED DESCRIPTION OF THE INVENTION

10   The invention provides new silsesquioxane polymers useful in photoresist or resist compositions, and is particularly useful in positive resist compositions. The invention also encompasses resist compositions containing silsesquioxane polymers mentioned above as well as methods of using such resist compositions in forming a patterned material structure on a substrate. More particularly, the silsesquioxane polymers of the invention comprise an acid labile moiety

15   comprising a cyclic ketal group.

The resist compositions of the invention are characterized in part by the presence of a silsesquioxane polymeric component, where:

(i) at least a portion of the polymeric component contains fluorinated
20   moieties,

(ii) at least a portion of the polymeric component contains pendant acid labile moieties comprising a cyclic ketal, which inhibit solubility of the resist in aqueous alkaline solutions, and

(iii) at least a portion of the polymeric component contains pendant polar
25   moieties which promote alkaline solubility of the resist in aqueous alkaline solutions.

The silsesquioxane polymeric component may have SiO moieties present as part of a polymer backbone or in groups which are pendant from the polymer
30   backbone. Preferably, the SiO moieties form part of a silsesquioxane polymer backbone structure. The silsesquioxane polymeric components preferably contain monomers of the structure:

$$\begin{array}{c} R \\ | \\ --SiO_x-- \end{array} \qquad (I)$$
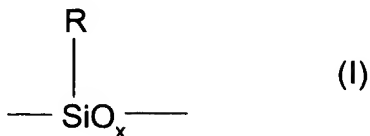
5

where x is about 1.5, and R is a group (i) at least a portion of which is fluorinated to increase transparency, and contains (ii) a polar moiety which promotes alkaline solubility of the resist in aqueous alkaline solutions, and (iii) an acid labile

10 moiety comprising a cyclic ketal which inhibits solubility of the resist in aqueous alkaline solutions.

Preferred solubility promoting polar moieties preferably include a hydroxyl or carboxylic acid moiety, more preferably a hydroxyl moiety. Solubility promoting

15 moieties in R may include sulfonamide, dicarboxyimide, N-hydroxy dicarboxyimide, any other amino group or any imino group. R may also include fluorinated versions of such solubility promoting moieties.

The solubility inhibiting acid labile cyclic ketal moieties are preferably pendant

20 from the backbone polymer and/or are provided in the polymer matrix as separate dissolution inhibitor molecules containing acid labile moieties. The acid labile cyclic ketal moieties are preferably cleavable in the presence of acid at a temperature at which image blur is minimized or avoided. In a preferred embodiment, the cyclic ketal moieties are cleavable in the presence of acid at

25 room temperature. Preferred cyclic ketal acid labile moieties are those classified as low activation energy (E_a) protecting groups (i.e. where E_a is less than about 20 kcal/mol).

Applicants have found that polymers protected with cyclic ketal moieties have

30 better inhibition of dissolution in an aqueous developer, such as an aqueous solution of tetramethyl ammonium hydroxide (TMAH), than those protected with linear ketals. For example, a polyhydroxystyrene containing 10% cyclohexanol units with a weight average molecular weight Mw ≈ 5700 was protected with 15%

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5   and 20% methoxypropene yielded polymers with dissolution rates of 215 Å/s and 115 Å/s, respectively, in 0.263N TMAH developer. The same polymer was protected with 17% and 18.5% methoxycyclohexene to yield polymers with dissolution rates of 3.8 Å/s and 2.3 Å/s respectively. Without intending to limit the present invention, it is believed that cyclic ketals have lower polarity than

10 linear ketals, and thus the use of cyclic ketal protecting groups would have improved inhibition of polymer solubility in an aqueous alkaline developer compared to polymers using linear ketal protecting groups. Since size and shape of protecting groups also affect solubility inhibition by their relative capability to block unprotected hydroxyl groups from contact with the developer.

15 Thus, it is believed that the shape of cyclic ketals will tend to block developer molecules, such as TMAH base ions, more efficiently than would linear ketal protecting groups.

Cyclic ketal protecting groups of the present invention may comprise structures

20 of the form:
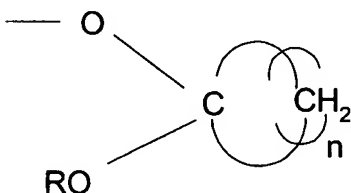
where n is any integer from 2 to 15, and R is an alkyl or halogenated alkyl.

25

Examples of preferred cyclic ketal protecting groups include, but are not limited to, unsubstituted cyclic aliphatic ketals that satisfy the above formula and thus can be employed in the present invention include:

30 methoxycyclopropanyl, ethoxycyclopropanyl, butoxycyclohexanyl, methoxycyclobutanyl, ethoxycyclobutanyl, methoxycyclopentanyl, ethoxycyclopentanyl, methoxycyclohexanyl, ethoxycyclohexanyl,

5   propoxycyclohexanyl, methoxycycloheptanyl, methoxycyclooctanyl,

methoxynorbornyl, methoxyadamantyl and the like. Of these unsubstituted cyclic

aliphatic ketals, it is highly preferred that methoxycyclohexanyl (MOCH) be

employed as the acid labile protecting group of the aqueous base soluble

polymer or copolymer.

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An oxygen atom may also be present within the cyclic ketal structure as long as

two oxygen atoms are attached to the same carbon, which then forms a cyclic

aliphatic ketal structure of the form:
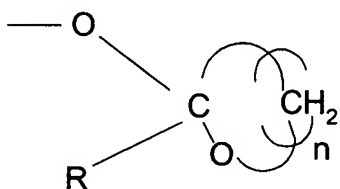
15

When the hydrogen of the cycloaliphatic portions of the ketal substituent is

substituted, it may be substituted with halogens and/or with hydrophobic groups,

so-called etch resistance groups or combinations or mixtures thereof. Examples

20   of hydrophobic groups that can be employed in the present invention are

halogen-containing groups such as —CF_3, —CHF_2, —$CH_2\,F$, —CCl_3, —$CHCl_2$

and —CH_2Cl, and silicon-containing groups such as —$Si(CH_3)_3$. When an etch

resistance group is employed, the hydrogen of the cycloaliphatic group may be

substituted with one or more of the following: metal-containing groups such as

25   Sn, Ti or Zn, and/or large bicyclic, tricyclic or other multicyclic groups containing

from about 6 to about 25 carbon atoms.

As stated above, some, but not all, of the initial hydroxyl or carboxylate functional

groups of the aqueous base soluble polymer or copolymer are protected with

30   said cyclic aliphatic ketal substituent. Typically, the aqueous base soluble

polymer contains from about 5 to about 95 mol % of said cyclic aliphatic ketal

protecting group and the remainder being the initial, unprotected functional
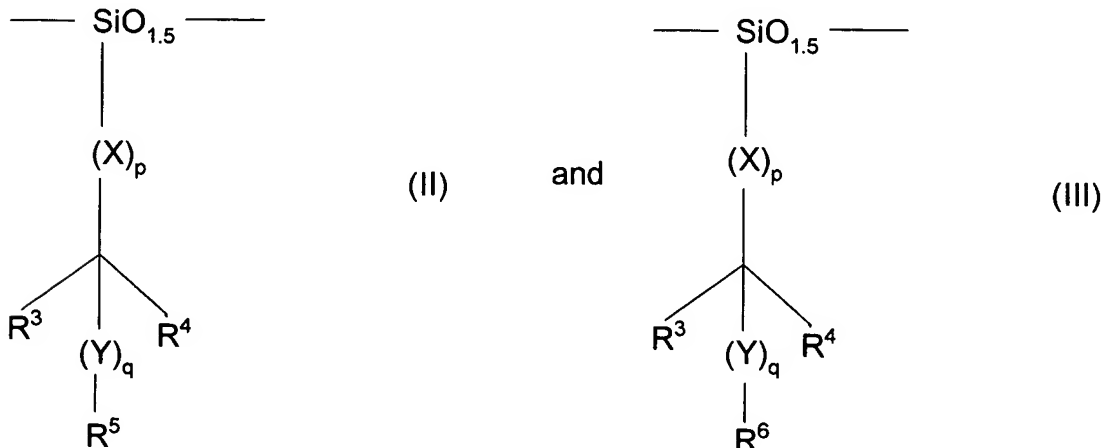
5 groups of the aqueous base soluble polymer or copolymer. More preferably, the aqueous base soluble polymer employed in the present invention contains from about 10 to about 50 mol % of said cyclic aliphatic ketal protecting group.

10 The silsesquioxane polymer preferably contains a combination of such monomers (I) having different R groups selected from (a)-(b). Thus, the silsesquioxane polymer of the present invention preferably contains one or more monomers selected from the group consisting of:

$$\text{(a)} \quad \begin{matrix} R^1 \\ | \\ -SiO_{1.5}- \end{matrix} \quad \text{and} \quad \text{(b)} \quad \begin{matrix} R^2 \\ | \\ -SiO_{1.5}- \end{matrix}$$

15 where R^1 contains a polar moiety that promotes alkaline solubility of the resist in aqueous alkaline solutions, and R^2 contains a cyclic ketal acid labile moiety that inhibits solubility of the resist in aqueous alkaline solutions. The silsesquioxane polymer preferably contains a combination of monomers (a) and (b). Preferably at least a portion of the silsesquioxane polymer is fluorinated, which may include

20 at least a fluorinated portion of monomers (a) and/or (b).

The novel silsesquioxane polymers of the invention preferably includes a combination of monomeric units (II) and (III) described by the formulas:

$$\begin{matrix} -SiO_{1.5}- \\ | \\ (X)_p \\ | \\ R^3 \diagup \! \big| \! \diagdown R^4 \\ (Y)_q \\ | \\ R^5 \end{matrix} \quad \text{(II)} \quad \text{and} \quad \begin{matrix} -SiO_{1.5}- \\ | \\ (X)_p \\ | \\ R^3 \diagup \! \big| \! \diagdown R^4 \\ (Y)_q \\ | \\ R^6 \end{matrix} \quad \text{(III)}$$

25

5

in which:

each R^3 is independently selected from any of a hydrogen atom, a halogen atom
(preferably fluorine), a linear or branched alkyl, a cycloalkyl, a halogenated linear

10 or branched alkyl (preferably a fluoroalkyl), a halogenated cycloalkyl (preferably a
fluorocycloalkyl), an aryl, a halogenated aryl (preferably a fluoroaryl), or any
combination thereof, and R^3 may optionally further include any of oxygen, sulfur
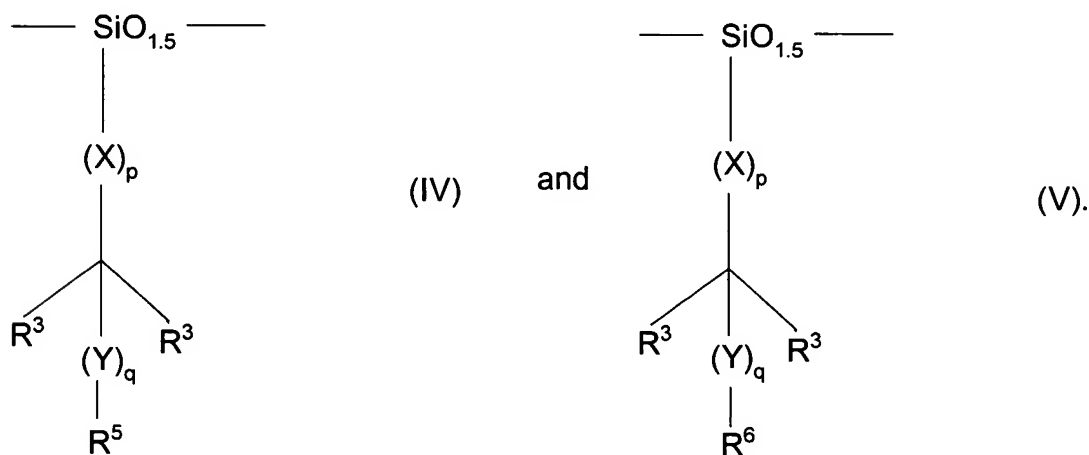or nitrogen;

15 each X is independently selected from any one of an oxygen atom, a sulfur atom,
NR^3, a linear or branched alkyl, a cycloalkyl group, a linear or a branched
halogenated alkyl (preferably a fluoroalkyl), a halogenated cycloalkyl (preferably
a fluorocycloalkyl), an aryl group, a halogenated aryl (preferably a fluoroaryl),
wherein p is an integer having the value 1 or 0 (i.e. including a single bond

20 between a silicon atom of the silsesquioxane group and a carbon atom of a side
group);

each Y is independently selected from any one of a linear or branched alkyl, a
cycloalkyl group, a linear or branched halogenated alkyl (preferably a fluoroalkyl),

25 a halogenated cycloalkyl (preferably a fluorocycloalkyl), an aryl group, a
halogenated aryl (preferably a fluoroaryl), wherein q is an integer having the
value 1 or 0 (i.e. R^3, R^4, R^5 bonded to the same carbon atom);

each R^4 is independently selected from any of fluorine, linear or branched

30 fluoroalkyl, fluorocycloalkyl, fluoroaryl, or any combination thereof, and R^4 may
optionally further include any of oxygen, sulfur or nitrogen, or any combination
thereof; and

R^6 represents an independently selected solubility promoting group. The

35 solubility promoting group is preferably a hydroxyl or coboxylic acid moiety, more

5   preferably a hydroxyl moiety, such as a fluoroalcohol. The solubility promoting

group may also be an imino group or an amino group, including, but not limited to

sulfonamide, dicarboxyimide, N-hydroxy dicarboxyimide phenol, or fluorinated

versions thereof.

10   R^5 represents an independently selected solubility inhibiting group comprising a

cyclic ketal which can be formed as a part of a pendant group from the

silsesquioxane structure. The cyclic ketal solubility inhibiting group may include

fluorinated versions thereof.

15   The novel silsesquioxane polymers of the invention may also preferably contain a

combination of monomeric units (III) and (IV) or units (II) and (V), where the units

(IV) and (V) are described by the formulas:

$$
\begin{array}{ccc}
\underline{\quad}\ SiO_{1.5}\ \underline{\quad} & & \underline{\quad}\ SiO_{1.5}\ \underline{\quad} \\
| & & | \\
(X)_p & & (X)_p \\
| & \text{(IV)} \quad \text{and} & | \\
R^3 \diagup | \diagdown R^3 & & R^3 \diagup | \diagdown R^3 \\
(Y)_q & & (Y)_q \\
| & & | \\
R^5 & & R^6
\end{array}
\qquad \text{(V).}
$$

20

The novel FSQ polymers of the invention preferably have a weight average

molecular weight of about 800 to 500,000, more preferably about 1,500 to

100,000, and most preferably about 1,500 to 10,000.

25   The properties of interest in this regard include solubility in aqueous alkaline

developers and a glass transition temperature (T_g) that is compatible with normal

thermal processing, such as post-apply bake (PAB) and post-exposure bake

5   (PEB). The T_g is preferably between 30 and 400 °C, more preferably between 50 and 300 °C, and most preferably between 70 and 250 °C. These properties are discussed further below in the discussion of resist compositions.

The radiation-sensitive or photosensitive acid generators (PAGs) used in the
10   resist compositions of the invention may be any suitable photosensitive acid generator known in the photoresist art, which is otherwise compatible with the other selected components of the resist composition, and in particular, for positive resist compositions. Examples of preferred photosensitive acid generators (PAG) include: —(trifluoromethylsulfonyloxy)-bicyclo[2.2.1]hept-5-
15   ene-2,3-dicarboximide ("MDT"), onium salts, aromatic diazonium salts, sulfonium salts, diaryliodonium salts and sulfonic acid esters of N-hydroxyamides or -imides, as disclosed in U.S. Pat. No. 4,731,605. Also, a PAG that produces a weaker acid such as dodecane sulfonate of N-hydroxy-naphthalimide ("DDSN") may be used. Fluorinated PAG is also preferred for better transparency at 157
20   nm. Another example of a preferred PAG includes a PAG containing a structure having the formula

$$R^7 \!-\!\!-\! \underset{\underset{Z^2}{|}}{\overset{\overset{Z^1}{|}}{C}} \!-\!\!-\! SO_2 \!-\!\!-$$
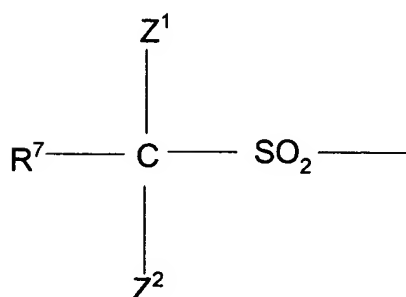
25   where R^7 is a monovalent organic group with a fluorine content of 50 wt% or less, a nitro group, a cyano group, or a hydrogen atom, and Z^1 and Z^2 are individually a fluorine atom or a linear or branched perfluoroalkyl group having 1-10 carbon atoms, as described in US Published Patent Application No. US 2003/0113658 A1, published June 19, 2003, the disclosure of which is incorporated by
30   reference. Combinations of PAGs may be used.

5

In addition to the above components, the resist compositions of the invention generally include a casting solvent to dissolve the other components so that the overall composition may be applied evenly on the substrate surface to provide a defect-free coating. Where the resist composition is used in a multilayer imaging

10 process, the solvent used in the imaging layer resist is preferably not a solvent to the underlayer materials, otherwise the unwanted intermixing may occur. When the underlayer composition uses a crosslinker approach, a cross-linked underlayer will prevent intermixing. In this case, the same or a different solvent can be used for both the imaging layer and the underlayer. Examples of suitable

15 casting solvents include: ethoxyethylpropionate ("EEP"), a combination of EEP and γ-butyrolactone ("GBL"), propylene-glycohnonoethylether acetate (PGMEA), and ethyl lactate. The invention is not limited to selection of any particular solvent.

20 The photoresist compositions may further include organic base additives, surfactants, sensitizers or other expedients known in the art. The compositions of the present invention are not limited to any specific selection of these expedients.

25 Examples of base additives include: dimethylamino pyridine, 7-diethylamino-4-methyl coumarin ("Coumarin 1"), tertiary amines, imidazoles, imides, amides, proton sponge, berberine, and the polymeric amines as in the PLURONIC® or TETRONIC® series from BASF. Tetra alkyl ammonium hydroxides or cetyltrimethyl ammonium hydroxide may be used as a base additive when the

30 PAG is an onium salt.

Examples of possible surfactants include fluorine-containing surfactants such as the FLUORAD™ series, preferably FC-430, and more preferably, FC-4430, both available from 3M Company in St. Paul, Minn., and siloxane-containing

35 surfactants such as the SILWET® series available from Union Carbide

5   Corporation in Danbury, Conn.

The resist compositions of the invention are not limited to any specific proportions of the various components. The resist composition of the present invention preferably includes about 0.1 - 25 wt. % PAG, more preferably about

10   0.5-15 wt. %, based on the total weight of imaging polymer in the composition. The inventive resist composition preferably contains about 0.02-8 wt. % of the base additive, more preferably about 0.1 - 2 wt. %, based on the total weight of acid sensitive polymer. Where the resist compositions of the invention contain a solvent, the overall composition preferably contains about 50-98 wt. % solvent.

15

The resist compositions of the invention are useful in single layer photolithographic processes, and are especially useful as imaging layers in multilayer photolithographic processes, such as bi-layer or tri-layer processes. Preferably, the resist compositions of the invention may be patterned using

20   various radiation types such as 365 nm wavelength, deep-UV (specifically 248 nm, and 193 nm wavelengths), extreme-UV (approximately 13 nm wavelength), x-ray, electron beam, and ion beam. The appropriate radiation type(s) may depend on the components of the overall resist composition (e.g., the selection of the polymer component, photosensitive acid generator (PAG), base (or

25   quencher), surfactant, solvent, etc.). The resist compositions of the invention generally provide high resolution (approximately 100 nm resolution or less) in combination with desired dissolution behavior.

The present invention encompasses a single layer method of forming a structure

30   on a substrate, including the steps:

       (a) providing a substrate;

       (b) applying a resist composition to the substrate to form a resist layer on
       the substrate, wherein the resist composition includes (i) an acid-sensitive
       imaging polymer, and (ii) a radiation-sensitive acid generator, wherein the

35   imaging polymer contains a silsesquioxane backbone, and a solubility

5   inhibiting pendant cyclic ketal acid-labile moiety having a low activation

energy for acid-catalyzed cleaving and wherein at least a portion of the

imaging polymer is fluorinated;

(c) patternwise exposing the substrate to radiation, whereby acid is

generated by the radiation-sensitive acid generator in exposed regions of

10   the resist layer;

(d) removing patternwise soluble portions of the resist layer to form a

pattern of spaces in the resist layer; and

(e) transferring the pattern of spaces to the substrate.

15   The exposed resist layer may be baked to promote an acid-catalyzed reaction in

the exposed portions of the resist layer.

The substrate may include a material layer to be patterned, and the method may

further include a step of transferring the pattern of spaces in the resist layer to

20   the underlying substrate by removing portions of the material layer through the

pattern of spaces in the resist layer. Alternatively, the method may include a step

of transferring the pattern of spaces in the resist layer to the underlying substrate

material (which may include one or more layers of material) by methods

including, but not limited to, depositing a material (such as an organic dielectric, a

25   metal, a ceramic or a semiconductor) onto the substrate at the spaces in the

resist layer, plating (such as electroless plating or electroplating), or implanting

dopants into the substrate material. The substrate may include any suitable

material useful in the formation of microelectronic structures, and is preferably

selected from any of an organic dielectric, a metal, a ceramic or a semiconductor.

30

The invention also encompasses a multilayer (e.g. using a bi-layer, tri-layer or

other multilayer resist structure) lithography method including the steps of: a)

forming a first layer of a planarizing material on a substrate; b) forming a second

(imaging) layer of a resist material on the first layer, wherein the second layer

35   includes a resist composition of the invention; c) pattern-wise exposing the

5   second layer to radiation using a patterning tool, optionally followed by post-exposure baking; d) developing a pattern in the second layer to remove unexposed portions of the second layer and to form a patterned resist that reveals portions of the first layer; and e) etching the underlayer through the patterned spaces in the second resist layer to expose the substrate surface. As

10   in a single layer method, the multilayer method may further include transferring the pattern of spaces in the multilayer resist to the underlying substrate by any conventional method such as depositing, implanting, plating or etching.

Preferably, the first layer is a planarizing underlayer that is highly energy

15   absorbing, and/or reduces reflection to the imaging resist layer. The planarizing underlayer is preferably applied directly over the material layer to be patterned. Subsequently, a layer of the inventive resist composition is applied over the first planarizing underlayer, using spin coating or other techniques. The resist coating is preferably as thin as possible provided that the thickness is preferably

20   substantially uniform and that the resist layer is sufficient to withstand subsequent processing (typically reactive ion etching (RIE)) to transfer the lithographic pattern to the planarizing underlayer. Optionally, the substrate with the resist coating may be heated (pre-exposure bake or post-apply bake (PAB)) to remove the solvent and improve the coherence of the resist layer. The PAB

25   step is preferably conducted for about 10 seconds to about 15 minutes, more preferably about 15 seconds to about two minutes. The PAB temperature may vary depending on the T_g of the resist.

The resist pattern is then patternwise exposed to the desired radiation. Where

30   scanning particle beams, such as electron beam, are used, patternwise exposure may be achieved by scanning the beam across the substrate and selectively applying the beam in the desired pattern. More typically, wavelike radiation, such as 193 nm or 157 nm UV radiation, is projected through a mask to provide patternwise radiation exposure to the resist. Preferably, the resist image formed

35   in the second layer is a high resolution resist image. Resolution enhancement

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5   techniques (RET), such as attenuated phase shift (attPSM), or alternating phase-shift (altPSM) masks or other RET methodologies, may be used as the radiation wavelengths decrease.

     Optionally, the patternwise exposed resist layer may be baked (post-exposure
10   bake or PEB) between the exposure and developing steps to further complete the acid-catalyzed reaction, to facilitate the deprotection of acid labile groups in the radiation-exposed portions of the resist layer and to enhance the contrast of the exposed pattern. The PEB is preferably conducted at about 10-175 °C, more preferably about 20-120 °C. The PEB is preferably conducted for about 30
15   seconds to 5 minutes.

     After post-exposure bake, the resist structure with the desired pattern is obtained (developed as in step (d)) by contacting the resist layer with an alkaline solution that selectively dissolves the areas of the resist which were exposed to radiation.
20   Preferred alkaline solutions (developers) are aqueous solutions of tetramethyl ammonium hydroxide (TMAH). Preferably, the step of developing the second layer uses an aqueous solution of TMAH of about 0.14 N or greater, more preferably about 0.20 N or greater, most preferably about 0.26 N or greater. The resulting lithographic structure on the substrate is then typically dried to remove
25   any remaining developer solvent.

     The portions of the first planarizing underlayer are preferably removed (i.e. to remove revealed portions of the first layer using remaining portions of the second layer as a mask) by etching. Preferably, the etching is performed by O_2 plasma
30   reactive ion etching (RIE) or other anisotropic etching techniques. Once the desired portions of the underlayer have been removed, the pattern may be transferred to portions of the substrate, for example, by etching (e.g., by reactive ion etching) the substrate at positions corresponding to the removed portions of the underlayer. Once the desired pattern transfer has taken place, any
35   remaining underlayer and resist may be removed by using conventional stripping

5   techniques.

The planarizing underlayer should be sufficiently etchable, selective to the overlying photoresist (to yield a good profile in the etched underlayer) while being resistant to the etch process needed to pattern the underlying material layer.

10   Additionally, the planarizing underlayer composition should have the desired optical characteristics (e.g., refractive index, optical density, etc.) such that the need for any additional antireflective coating (ARC) layer is avoided. The planarizing underlayer composition should also have physical/chemical compatibility with the imaging resist layer to avoid unwanted interactions which

15   may cause footing and/or scumming. Preferably, the planarizing underlayer compositions are characterized by the presence of (A) a polymer containing: (i) cyclic ether moieties, (ii) saturated polycyclic moieties, and (iii) aromatic moieties for compositions not requiring a separate crosslinker, or (B) a polymer containing: (i) saturated polycyclic moieties, and (ii) aromatic moieties for

20   compositions requiring a separate crosslinker, as described in US Published Patent Application No. US 2002/0058204 A1, published May 16, 2002, the disclosure of which is incorporated herein by reference. Most preferably, a portion of the above-mentioned planarizing underlayer composition further comprises fluorinated polycyclic moieties and/or fluorinated aromatic moieties.

25

The following examples are provided to further describe the present invention. The invention is not limited to the details of the examples.

EXAMPLE 1

30

Comparison of Resists Formulated with Three Different Polymers

Polymer 1. Poly(2-hydroxy-3,3,3-trifluoropropylsilsesquioxane) (FSQ) was partially protected with 40 mole % of methoxycyclohexene (MOCH).

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5   Polymer 2. Poly(2-hydroxy-3,3,3-trifluoropropylsilsesquioxane) (FSQ) was partially protected with 44 mole % of ethyl vinyl ether (EVE).

    Polymer 3. Poly[2-hydroxy-3,3,3-trifluoropropylsilsesquioxane-co-5-(2-t-butoxy-carbony)norbonylsilsesquioxane]

10   with the following formulation in PGMEA solvent:

    3 wt% relative to the polymer TPStTrf (triphenyl sulfonium triflate)

    4 wt% relative to the polyer TBAH (tetrabutyl ammonium hydroxide)

    200 ppm FLUORAD™ FC-430 surfactant (available from 3M Company).

15

    Resists formulated with polymers 1 and 3 were spin coated on AR40 (from Shipley Company) ARC coated wafers. The films were baked on a hot plate at 110 °C for 1 minute. The exposures were performed on an ASML PAS 5500/1100 tool with an NA of 0.75 using an attPSM mask. After exposure, the

20   resists were baked at 90 °C for 1minute before being developed with 0.263 N TMAH for 60s. Images of 90nm lines with 180nm pitch were resolved for the resist formulated with polmer 1 but not the resist formulated with polymer 3.

    Resists formulated with polymers 1 and 2 were spin coated on HMDS

25   (hexamethyldisilazane) primed wafers. The films were baked on a hot plate at 100 °C (polymer 1 resist) and 110 °C (polymer 2 resist), respectively, for 1 minute. The exposures were performed on a 100 kV Leica exposure system. After exposure, the polymer 1 resist was allowed to sit in the regular lab environment for 30 minutes without PEB. The polymer 2 resist was processed

30   under two conditions: 1) a polymer 2 resist was allowed to sit in the regular lab environment for 30 minutes without PEB; and 2) a polymer 2 resist was baked at 90 °C for 1 minute. Both the polymer 1 and 2 exposed resists were developed with 0.263 N TMAH for 60s. High resolution of 30nm l/s images was obtained on polymer 1 resist but not on the polymer 2 resists using either the bake or no bake
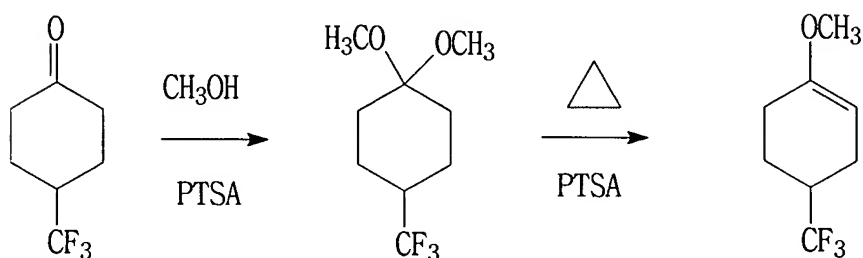
35   process.

5

EXAMPLE 2

Synthesis of a Fluorinated Cyclic Ketal Protecting Group

10   A new fluorinated cyclic ketal protecting group with the structure:
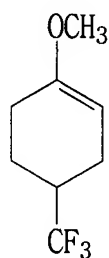
was synthesized using the following synthetic scheme:

15

Approximately 5g of 4-(trifluoromethyl)cyclohexanone was placed in a 25g flask
with 20mg p-toluenesulfonic acid monohydrate (PTSA) and 10g of absolute
methanol. The flask was then heated up to about 72 °C for 2 days with a heating

20   mantel. The methanol and water were then distilled off at 70 °C with a vacuum
pump. Approximately 10g of absolute methanol was then added into the
remaining solution again, and the solution was allowed to reflux at 90 °C for 2 ½
hours. The methanol was distilled off at 70 °C under vacuum for a few hours.
The temperature was then raised to 100 °C to collect the distilled liquid.

25   A nuclear magnetic resonance (NMR) analysis shows the final distilled
compound has ~90% 4-trifluoromethyl-1-methoxycyclohexene and ~10% of 4-
trifluoromethyl-1,1-dimethoxycyclohexane.

5

EXAMPLE 3

Synthesis of FSQ with protecting groups of ethoxycyclohexene (EOCH) and
methoxypropene (MOP), protected poly(2-hydroxy-3,3,3-

10   trifluoropropylsilsesquioxane), resulting in FSQ protected polymers FSQ-EOCH
and FSQ-MOP respectively. Resists were formulated and evaluated with these
polymers.

20 wt. % poly(2-hydroxy-3,3,3-trifluoropropylsilsesquioxane) in PGMEA solution

15   was added in with oxalic acid. After the acid was dissolved, the protecting
groups were added to the solution, and the reaction was carried out at room
temperature with stirring overnight. The quantities of materials used in the
synthesis are listed in the Table 1 below. All the reactions were quenched with
1.5g of Al_2O_3.

20

TABLE 1

Polymer	FSQ (20% solid)	Protecting group	catalyst	NMR
FSQ-EOCH	10g	0.85g ethoxycyclohexene	~10mg oxalic acid	8% protection
FSQ-MOP	12g	0.56g methoxypropene	~5mg oxalic acid	15% protection

Resist formulations were obtained by mixing partially protected polymers (from
TABLE 1) with 0.4 wt. % (relative to the polymer) tetrabutyl ammonium hydroxide

25   (TBAH) and 3 wt. % triphenylsulfonium triflate (TPS TRF) and 200-1000 ppm of
FLUORAD™ FC-430 surfactant (available from 3M Company) in PGMEA
solvent. The total solid weight content in the solution was about 14%. The
resists were spin coated on hexamethyldisilazane (HMDS) primed wafers. The

5 films were baked (post-apply bake or PAB) on a hot plate at 90-110°C for 1
minute.

The exposures were performed at 25 kV on a ElectronCure™-200M tool
manufactured by Electron Vision Group. After exposure, resists were either

10 baked at 90-110 °C for 1 minute or rested for 30 minutes without post-exposure
bake (PEB) before being developed with 0.26N TMAH for 60-75s. The following
Table 2 lists the dose to clear a large square exposed using resist formulations
with different acetal and ketal protected polymers and the corresponding film
loss. It shows that a resist formulated with a polymer having only 8% protection

15 with a cyclic ketal has less film loss in comparison to a resist formulated with
15% protection with a linear ketal.

TABLE 2

Polymer in the resist formulation	Process conditions	Dose to clear	Film Loss
FSQ-EOCH	1500rpm, 110 °C/60s PAB and NO PEB, 0.26N TMAH 60s	$6\mu C/cm^2$	503 Å
FSQ-MOP	1500rpm, 90 °C/60s PAB and NO PEB, 0.26N TMAH 75s	$8\mu C/cm^2$	840 Å

20

While the invention has been particularly shown and described with reference to
preferred embodiments thereof, it will be understood by those skilled in the art
that various changes in form and details may be made therein without departing
from the spirit and scope of the invention.

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